



NRL Memorandum Report 5961

(2)

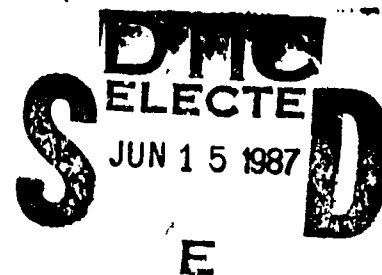
## **Microsensor Monitoring of Engine Lubricants for Fuel Dilution and Water Content**

**ROBERT N. BOLSTER**

*Surface Chemistry Branch  
Chemistry Division*

May 20, 1987

AD-A181 287



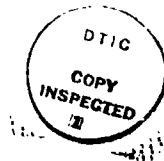
## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 5961			7a. NAME OF MONITORING ORGANIZATION	
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory		6b. OFFICE SYMBOL (If applicable) Code 6170	7b. ADDRESS (City, State, and ZIP Code)	
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U.S. Army Belvoir Res., Dev. and Eng. Center		8b. OFFICE SYMBOL (If applicable) STRBE-VF	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) Ft. Belvoir, VA 22060-5606			PROGRAM ELEMENT NO. 62104A	PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Microsensor Monitoring of Engine Lubricants for Fuel Dilution and Water Content				
12. PERSONAL AUTHOR(S) Robert N. Bolster				
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM 4/84 TO 10/86	14. DATE OF REPORT (Year, Month, Day) 1987 May 20	15. PAGE COUNT 26	
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	Fuel dilution Lubricant sensor	
			Engine lubricant	
			Lubricant monitor	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>A laboratory device has been developed to examine diesel engine lubricants for fuel dilution. Samples of 25 microliters were heated in flowing air, and the volatiles evolved were detected with a calibrated electronic sensor. With suitable temperatures and flow rates, determined from tests of typical lubricants and fuels, dilution of 1% was readily detectable. The quantitative precision of the method was affected by the varied oil volatilities, but was limited by the stability of the semiconductor sensor. Moisture sensitivity, flow rate sensitivity, and slowness in returning to its baseline level after use were encountered. A surface acoustic wave fuel sensor might offer improved performance. The detection of small quantities of water in lubricants by this method is difficult, due to the small sample volume and interference by the organic vapors, but should be possible with sensitive and discriminating sensors.</p>				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> OTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Robert N. Bolster			22b. TELEPHONE (Include Area Code) (202) 767-2920	22c. OFFICE SYMBOL Code 6170

## CONTENTS

INTRODUCTION .....	1
EXPERIMENTAL APPARATUS AND PROCEDURES .....	2
Cell and Heater .....	2
Sensors and Data Collection .....	3
Procedure .....	4
Materials .....	5
RESULTS AND DISCUSSION .....	6
Sensor Calibration .....	6
Determination of Apparatus Parameters .....	8
Volatility Determinations .....	8
Tests of Fuel and Lubricant Mixtures .....	10
Quality of the Results .....	13
Water Sensor .....	15
CONCLUSIONS .....	15
REFERENCES .....	16

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



# **MICROSENSOR MONITORING OF ENGINE LUBRICANTS FOR FUEL DILUTION AND WATER CONTENT**

## **INTRODUCTION**

The useful life of the lubricating oil in an internal combustion engine is usually limited by the accumulation of foreign matter rather than by degradation of the base fluid or even depletion of the additives. Two foreign materials often found in diesel engines are fuel and water. These may come from leakage within the engine or from blow-by vapors from the combustion chambers. Fuel dilution in excess of 5% may reduce the viscosity of the lubricant so that hydrodynamic films in heavily loaded areas become too thin to separate the moving parts, and wear increases. Water promotes corrosion, and is of concern when present in more than a few parts per thousand.

The development of electronic chemical microsensors in recent years has opened up the possibilities for monitoring lubricant composition simply and directly rather than by chemical analyses or measurements of physical properties such as viscosity. Information on the condition of an engine's lubricant not only helps to determine when the lubricant needs to be changed, but can also provide warning of mechanical problems, such as leaking fuel injector piping or gaskets, before the lubricant's properties are seriously affected.

In a research proposal (1) Wohltjen suggested the use of microsensors to measure fuel dilution and water in lubricants by heating a small sample in a gas stream and detecting the resulting hydrocarbon and water vapors in the gas. The aim of this work

was to develop a laboratory device and determine the feasibility of the technique. If successful, this would lead to a prototype of a field-deployable unit.

An in situ real-time monitor is not contemplated. While this might be feasible for water detection, the presence of gaseous combustion products in an operating engine and the variable temperatures preclude the use of hydrocarbon vapor detectors. In the fluid phase there is presently no simple means of detecting fuel in the presence of the lubricant if both are hydrocarbons.

## EXPERIMENTAL APPARATUS AND PROCEDURES

### Cell and Heater

The heart of the laboratory device to evaluate the proposed fuel dilution and water detection method was a cell and sample heater constructed as shown in Fig. 1. The cell body and lid were machined from aluminum, with thick walls to provide a uniform and constant interior temperature. An electrical heater, wrapped around the cell and powered by a temperature controller, maintained the cell walls above the ambient temperature to prevent condensation of the fuel and water vapors after evolution. The cell volume was 16 ml.

The sample heater was a boat formed from a thin nickel strip. Heavy copper wires supported it in the cell and connected it to a high-current 360:1 transformer. To prevent the sample from spreading away from the boat, the ends of the strip were made narrower than the center to make them slightly hotter, and they extended upward from the boat. The resistance of the heater was 1.7 milliohms, and it produced about 12 watts of heat with 50 V applied to the transformer. The temperature of the sample was measured with a thermocouple extending down from the lid to contact the center of the boat. A programmable time-proportioning temperature controller was used to regulate the current to the heater. This device provided stepped or ramped increases in temperature, and was tuned to the heater characteristics to give a rapid temperature rise with little

overshoot. The sample temperature could be brought from 25 to 130°C in 15 s with an overshoot of 3°. Fuel and lubricant samples 5 to 50 µl in volume were dispensed into the boat from microliter syringes.

Air flowing at 50 to 200 ml/min entered the cell at the bottom and carried the vapors out a tube near the top to the sensors. Ambient air was used, supplied by a low-pressure pump. Dry air was provided by interposing a trap cooled by solid carbon dioxide.

### Sensors and Data Collection

The sensor used to detect the hydrocarbon vapors was a commercially-available tin oxide chemiresistor. The sensor and its electronic circuitry were described in reports (2), (3) on its use as a detector of lubricant oxidative breakdown products. The sensor consisted essentially of a ceramic cylinder a few mm long containing a heating filament and coated on the outside with a sintered layer of tin oxide with proprietary catalysts. Two electrodes made contact with the oxide surface, the resistivity of which decreased when exposed to organic vapors. The electronics consisted of a regulated power supply for the heating filament and a two-stage current amplifier to provide an output signal.

In the course of this work the circuit was modified by removal of the 6 ohm resistor in the sensor power supply. This increased the sensor temperature and bias potential, raising its sensitivity to hydrocarbon vapors.

The sensor was calibrated by placing it in a closed flask at a known temperature with dry air and a few drops of one of a series of pure normal aliphatic hydrocarbon liquids. The concentrations were calculated from the known vapor pressures. The water sensitivity was determined by placing the sensor in a closed flask containing air saturated with water vapor, exposing it to air having a known relative humidity, or placing it in flowing air having a controlled water vapor concentration.

The water sensor was a surface acoustic wave (SAW) device having a 112 MHz dual-channel quartz crystal. The sensor and computer interface were constructed by Microsensor Systems, Inc. One channel was coated with a film of poly(vinyl pyrrolidone) to absorb moisture from the air stream. The frequency difference between the two channels varied with the moisture concentration. Difficulties with the design, construction, and operation of this device have delayed its implementation, and it is not yet integrated into the system.

Data from the thermocouple that measured the sample temperature and the hydrocarbon sensor were digitized, collected every 5 s, stored, and displayed by a microcomputer. Software has been written to collect and display the raw data in real time, and to calculate, display, and plot the concentration-vs.-time results using the sensor calibration parameters. Peak and integrated concentration results were provided. Concentration vs. temperature plots could be made when ramped temperature increases were used. The data were stored on magnetic diskettes for later review and analysis.

### Procedure

In preparation for test runs, the cell temperature and air flow rate were brought to the desired levels, usually 60°C and 100 ml/minute. The sample heating boat was cleaned and briefly heated to drive off any residual volatiles from previous tests, and the temperatures and sensor readings were allowed to stabilize.

For stepped temperature tests, one minute of this baseline condition was recorded, the cell was opened and the sample was placed in the boat, and another minute was allowed for conditions in the cell to stabilize. The sample temperature controller was then turned on to heat the boat rapidly, typically to 130°C. The rise and decline of the sensor signal was recorded for 5 minutes, the sample heat was turned off, and another 3

minutes of data were collected. The computer then reduced the sensor data to concentration, plotted the temperature and concentration vs. time curves, and provided the maxima, integrated concentration, and time data.

Ramped temperature tests were made with different sample volumes depending on the volatility: 20  $\mu$ l for oils and 5  $\mu$ l for fuels. After introduction of the sample the boat temperature controller was turned on, usually set to raise the temperature at 10<sup>o</sup>/minute to 180<sup>o</sup>C. Lubricants gave satisfactory profiles with a more rapid rise of 20<sup>o</sup>/minute due to their lower volatilities. The computer again provided concentration and temperature vs. time plots, and a plot of concentration as a function of temperature.

### Materials

The lubricants, fuels, and pure hydrocarbons used are listed in Table 1 with military specification numbers. Samples of the lubricants and the DF-1 fuel were provided by the U.S. Army Belvoir Research, Development and Engineering Center.

TABLE 1  
Lubricant and Fuel Samples and  
Calibrating Hydrocarbons

#### Lubricants

MIL-L-2104D, Grade 10  
MIL-L-2104D, Grade 30  
MIL-L-2104D, Grade 40  
MIL-L-2104D, Grade 15W-40  
MIL-L-46167, Arctic Engine Lubricant

#### Fuels

VV-F-800C, Grade DF-1, Winter Diesel Fuel  
VV-F-800C, Grade DF-2, Regular Diesel Fuel  
MIL-F-16884H, Diesel Fuel, Marine (DFM)  
VV-F-815D, Fuel Oil, Burner, No. 2 (FO-2)  
MIL-T-5624L, Turbine Fuel, Grade JP-5

#### Pure Hydrocarbons

Normal Decane, C<sub>10</sub>H<sub>22</sub>, 99%  
Normal Undecane, C<sub>11</sub>H<sub>24</sub>, 99%  
Normal Tridecane, C<sub>13</sub>H<sub>28</sub>, 99%



## RESULTS AND DISCUSSION

### Sensor Calibration

The relationship between the tin oxide gas sensor signal and concentration, and the means of fitting the calibration curve for alcohols and ketones have been previously described (2), (3). The sensors were less sensitive to fuel and lubricant hydrocarbons than to these oxygen-containing organic compounds, and higher sensitivity was needed to detect the vapors from small samples. Increasing the voltage supplied to the sensors to 5 V increased their sensitivity by raising both the temperature and the bias potential. The calibration curve was found to be linear when plotted as a power-law function of  $\log (C+N)$  vs.  $\log (10.78/(5.78-E)-1)$ , where E was the signal, C was the concentration in parts per thousand (ppt), and N was a constant. The slope of the fitted line and the intercept gave the values of M and B as before (2), (3). The three parameters defining the performance of a given sensor in one class of organic vapor were derived from these:  $\text{Beta} = 1/M$ ,  $K = 1/N$ , and  $R_0 = 10^4 (BK)^{\text{Beta}}$ .

Shown in Fig. 2 are calibration curves for water and hydrocarbons for both voltages. Not only was the hydrocarbon sensitivity increased, but also the sensitivity relative to that for water, reducing the problem of correcting for the water interference.

The sensitivity of the tin oxide sensor to water was still a problem, however, as the concentration derived from the signal with a mixture of water and hydrocarbon vapor was several times higher than the sum of the same concentrations measured separately. Thus, the equation for the sensor response may have both additive and multiplicative terms, as was noted by Clifford and Tuma (4) for water and carbon monoxide. For a single class of organic compounds, the sensor resistance should fit the relationship:

$$R_s = R_0 (1 + K_0 C_0)^{-\text{Beta}}$$

where  $R_s$  is the resistance,  $R_0$  is the resistance in pure, dry air,  $K_0$  and Beta are the calibration constants for the sensor, and  $C_0$  is the concentration of the organic vapor.

With water also present, the resistance might be:

$$R_s = R_0 (1 + K_0 C_0 + K_w C_w + K_{ow} C_0 C_w)^{-\text{Beta}}$$

where  $K_w$  is the constant for water,  $C_w$  is the water vapor concentration, and  $K_{ow}$  is a combined organic and water constant. Theoretically,  $K_0$  and  $K_w$  can be found from separate calibrations, and then  $K_{ow}$  from a known mixture. In practice, the accumulation of experimental errors makes this difficult. Also, though the equation requires that Beta and  $R_0$  be the same for water and organics, separate calibrations always gave smaller Betas for water.  $R_0$  also was found to vary considerably.

One reason found for the calibration problems was the effect of air flow rate on the sensor signals. Not only did the signal change with flow rate, but in opposite directions in dry and moist air. Increased dry air flow decreased the signal, apparently by cooling the sensor surface and thus increasing its resistance. Increased flow of moist air increased the signal, apparently due to increased mass transfer to the surface. A series of water calibration measurements was made under controlled flow conditions, but the hydrocarbon calibrations were done inside a flask, where the flow was not controlled.

The constants for the sensor used in most of this work are given in Table 2. The water data were taken with an air flow of 100 ml/min. with the sensor in a tube with an inside diameter of 20.54 mm. The resistance,  $R_0$ , varied from 107 to 206 kohm over all of the calibrations made. At the lower voltage it was several times higher: 300 to 750 kohm.

Table 2  
Sensor Constants

	K ppt <sup>-1</sup>	Beta	R <sub>0</sub> kohm
Organic (Hydrocarbons)	430	0.51	130
Water	0.56	0.39	110

The speed of response of the tin oxide sensor to increasing concentrations of vapors was adequate. The concentration reading typically reached 50% of the ultimate value in 10 to 20 s, and reached 90% in 30 to 90 s.

The rate of return of the signal to its baseline level was more troublesome. The decay of the concentration reading was usually proportional to the reciprocal of the elapsed time. Thus, if the reading was  $C$  after time  $t$ , then to reach  $C/n$  would require a total time of  $n \times t$ . The baseline error was thus  $m/t$  where  $m$  was the slope of the plot of  $C$  vs.  $1/t$ . When  $C$  was in parts per million (ppm) and  $t$  was in seconds,  $m$  was typically 7000 to 22,000, the larger value being associated with a higher starting concentration. After exposure to a very high concentration of 20,000 ppm, 15 to 20 minutes were required for the reading to reach an acceptable error of 50 ppm, and 3 minutes were required after exposure to 350 ppm. During test runs, levels of 300 to 5000 ppm were encountered. The slow recovery thus introduced some errors into subsequent test runs, and limited the rate at which tests could be made.

#### Determination of Apparatus Parameters

To find the optimum operating conditions, a lubricant with 5% fuel was tested at 4 cell temperatures, 3 air flow rates, and 2 sample volumes. Higher cell temperatures gave higher and sharper peak concentrations and higher integrated concentrations by preventing condensation of the vapors, but also gave higher baseline levels. High flow rates gave lower peak and integrated concentrations by diluting the vapors, but gave more rapid response. Standard conditions of 60°C cell temperature and 100 ml/minute air flow rate were chosen. Sample volumes of 10 and 25 microliters appeared equally satisfactory, producing proportional responses.

#### Volatility Determinations

To determine the volatilities of the various diesel engine lubricants and fuels, test runs were made with ramped temperature increases. The plots of concentrations vs.

temperature showed the temperatures at which the fuels produced the greatest vapor concentrations, and at which the lubricants began to produce interfering concentrations.

The data for five lubricants are plotted in Fig. 3. The four lubricants qualified under specification MIL-L-2104D all showed relatively low volatilities until the temperature reached 150°C. The lower-viscosity oils would be expected to be more volatile, and this appeared to be true at the highest temperature. The Grade 30 oil was apparently a blend or a wide distillation cut, as it was more volatile at low temperatures than the less viscous Grade 10. The arctic oil of MIL-L-46167 apparently contained a volatile component, perhaps to reduce its viscosity so that it could be poured from the container at low temperatures. This might give a false indication of fuel dilution until it evaporated from the crankcase, but it appears to be only 2 to 3% of the lubricant.

The plots of data for similar measurements of diesel fuels, JP-5, and No. 2 Fuel Oil are shown in Fig. 4. All of these fuels showed peak vapor concentrations between 70 and 90°C. The JP-5 and DF-1 were narrower cuts, having higher peak concentrations followed by steeper slopes when compared with the DF-2 and FO-2. Two pure aliphatic hydrocarbons of similar volatility were also measured to determine the sharpness of the peaks. The resulting plots are shown in Fig. 5. Undecane produced a fairly sharp peak with a maximum at 80°. The tridecane maximum was at 100 to 105° and much broader, presumably due to condensation on the cell walls. The linear decline after the peak was probably due to wall evaporation. Increasing the cell temperature sharpened the peak considerably. These peaks were due to evaporation, not boiling, as the boiling points of the compounds were 196 and 234°C. The concentrations detected were considerably higher than for the fuels, which apparently contained substantial amounts of higher-boiling fractions. Diesel fuel is composed roughly one half of fractions boiling above 260°. Thus, the peaks in Fig. 4 represent only the most volatile fractions.

A sample heater temperature of 130°C was selected as optimum, as all of the diesel fuels showed peak concentrations well below this point and the lubricants' vapor concentrations did not rise sharply until 150° or higher.

#### Tests of Fuel and Lubricant Mixtures

Fifteen mixtures of lubricants with diesel fuels DF-1 and DF-2 were prepared, with either 1 or 5% fuel by volume. These and the neat lubricants were subjected to testing with a stepped temperature increase under standard conditions: 60° cell temperature, 100 ml/minute dry air flow, 25 µl sample volume, and rapid sample temperature rise to 130°.

Figure 6 shows computer-plotted results from some of the test runs. The small concentration peaks at 1 minute were caused by the opening of the cell to inject the sample. The large peaks were due to the volatiles evolved when the sample heater was turned on at 2 minutes, as shown by the temperature plot in Fig. 6 (b). The peak then decayed as the volatiles were depleted. An increase in slope is seen after 7 minutes, when the heater was turned off. Plots for the neat 15W-40 lubricant and the same oil with 5% DF-1 are shown superimposed in Fig. 6(d) to show the increase in vapor concentration due to the fuel dilution.

In order to determine the effect of the sensor's slowness in returning to its baseline level, four consecutive test runs with the 15W-40 lubricant were made. Peak and integrated concentrations were plotted against the starting baseline level, and correction factors were calculated from the best fitted straight lines. The corrections to be subtracted were found to be 2.03 and 11.9 (for 10 minutes) times the starting baseline for the peak and integrated concentrations, respectively. The baselines for all of the test runs ranged from 2 to 101 ppm, or 210 to 1010 ppm-minutes when integrated over 10 minutes. The corrections reduced all of the data to a zero-baseline condition.

The integrated concentration data showed less scatter than the peak data, as well as a better fit to the baseline correction. These results for 23 test runs, including three replicates, are shown in Table 3. In the upper half of the table are the integrated concentrations, corrected for baseline changes. The concentrations for the neat lubricants correlate well with those of Fig. 3 at 130°, and were higher when fuels were added. In the lower half of Table 3 are the responses for equal fuel additions, calculated from the concentrations by subtracting that for the neat lubricant and then dividing by the fuel content in %. The means and standard deviations for the rows and columns were then calculated, with the 5% data given a weighting factor of 5. The differences in response to the two fuels and two amounts are not significant, but those due to the different lubricants are. They appear to have an inverse correlation with the data of Fig. 3 at a higher temperature of 150 to 160°. That is, the more volatile lubricants gave lower fuel responses. This may have resulted from an over-correction when the neat lubricant vapor concentrations were subtracted.

TABLE 3  
Results with Known Lubricant and Fuel Mixtures

		Lubricant					
Fuel	Amount, %	MIL-L-46167	MIL-L-2104D			Mean	
		10	30	15W-40	40		
<hr/>							
Integrated concentrations, ppm-minutes							
-	0	3050	1410	2160	700	840	
				2090	950		1600
<hr/>							
DF-1	1	4040	2770	2590	1750		
DF-2	1			2930	1690	2040	
				3030			
<hr/>							
DF-1	5	7870	4560	4980	5710	7510	
DF-2	5			4820	5060	6110	
<hr/>							
Fuel Response, ppm-minutes / %							
DF-1	1	990	1360	470	920		940 ± 370
DF-2	1			810	860	1200	940 ± 170
				910			
<hr/>							
DF-1	5	960	630	570	980	1330	900 ± 310
DF-2	5			540	850	1050	810 ± 260
<hr/>							
Mean Response		970	750	600	910	1190	880 ± 260
		± 10	± 300	± 120	± 60	± 140	
<hr/>							

The data can be reduced to yield percent fuel dilution using the mean response of 880 from Table 3 and the mean of the concentrations from the lubricants (1600) to see how much variation there is in the results. The found fuel percentages and errors are given in Table 4. The results were a bit ragged with 1% fuel, but were not too bad at 5%. The greatest error was 2.1% fuel, 42% above the correct value. This was with the 46167 lubricant, which contained a volatile fraction. The standard deviations of the amounts found were 0.9 at 1% and 1.4 at 5%. The mean absolute errors (averages neglecting the sign of the error) were 71 and 24% for the low and high fuel mixtures.

TABLE 4  
Found Fuel Amounts and Errors  
with General Correction

		Lubricant					
Fuel	Actual Amount, %	MIL-L- 46167	MIL-L-2104D				Mean
			10	30	15W-40	40	
-----							
Amount of Fuel Found, % ((Conc. - 1600) / 880)							
	0	1.6	0.2	0.6 0.6	1.0 0.7	0.9	0.0
-----							
DF 1	1	2.8	1.3	1.1	0.2		1.4
DF 2	1			1.5 1.6	0.1	0.5	0.9
-----							
DF 1	5	7.1	3.4	3.8	4.7	6.7	5.1
DF 2	5			3.7	3.9	5.1	4.2
-----							
Error, % of Actual Amount Fuel (100 (Found - Actual) / Actual)							
DF 1	1	180	33	13	83		36
DF 2	1			52 62	90	51	7
-----							
DF 1	5	42	33	23	7	34	3
DF 2	5			27	21	3	15
-----							
Mean Error		110	0	15	50	5	5

When individual values for the neat lubricants were used in the reduction, the results were improved. This method would require that the characteristics of the lubricant in each sample be known, information which might be unobtainable in practice.

These results are shown in Table 5. Some of the larger errors were corrected by this treatment, in particular, those due to the 46167 lubricant. The errors in the determinations of the 1% fuel mixtures were considerably reduced, but those for 5% were essentially unchanged. The standard deviations for the amounts found at 1% and 5% were 0.3 and 1.6% fuel, and the mean absolute errors were 21 and 25%.

TABLE 5  
Found Fuel Amounts and Errors  
with Individual Corrections

		Lubricant					
Fuel	Actual Amount, %	MIL-L- 46167	MIL-L-2104D				Mean
			10	30	15W-40	40	
Amount of Fuel Found, % ((Conc. - Neat) / 880)							
DF-1	1	1.1	1.6	0.5	1.1		1.1
DF-2	1			0.9	1.0	1.4	1.1
1.0							
DF-1	5	5.5	3.6	3.3	5.6	7.6	5.1
DF-2	5			3.1	4.8	6.0	4.6
Error, % of Actual Amount Fuel (100 (Found - Actual) / Actual)							
DF-1	1	14	55	-47	5		7
DF-2	1			- 8	-1	36	8
3							
DF-1	5	10	-28	-35	-11	52	2
DF-2	5			-38	- 4	20	-7
Mean Error		12	14	-25	3	36	3

#### Quality of the Results

Although the errors shown in Table 5 might be marginally acceptable in the performance of a unit in the field, they are excessive for a device operated under laboratory conditions, especially when the sample set contained the standards used to calibrate the system. The basic technique appears to be satisfactory. Although subject to some uncertainties due to differences in various grades of lubricants and fuels, it appears capable of detecting fuel dilution of 1%, well below critical levels.



The principal shortcoming of the present implementation was in the accuracy of the gas sensor. The tin oxide sensor, although simple and rugged, suffered from several problems which made it difficult to calibrate accurately and reduced its repeatability. The signal was slow in returning to its baseline level after exposure to organic vapors, and large concentrations resulted in very long recovery times and sometimes permanent changes. The sensitivity to water vapor and its complex synergistic effect with organics required the use of dried air, and would cause problems if samples containing water were tested. The change in signal with change in flow rate complicated the calibration process.

The surface acoustic wave sensor might offer improved stability as a hydrocarbon detector. This device is under development at NRL and elsewhere as a chemical sensor (5), (6). The resonant frequency of the SAW crystal is altered by the mass of the coating, which can be made to selectively absorb components of the surrounding atmosphere, increasing the coating's mass. The frequency shift is proportional to the concentration of the vapor. The linear response makes calibration simpler and improves the precision, though it reduces the range. The SAW sensor operates at ambient temperature, so it should not be sensitive to flow rate changes. The response speed depends on the coating thickness, but is generally better than that of the tin oxide sensor. Baseline rise and drift should be reduced, but care might have to be taken to prevent any condensation of vapors on the sensor coating. Although perfect selectivity may not be attainable, interferences by other vapors are not complex, as they are with the tin oxide sensor, and may thus be compensated for more easily. Since the coating can be removed and replaced, its composition and thickness can be tailored to optimize the sensor performance.

A recent study of coatings for SAW sensors (7) showed that poly(isoprene) might be suitable for a hydrocarbon sensor. Although its normalized response to the hydrocarbon

isooctane was not very great, it was 19 times higher than the water response. This should provide adequate discrimination against water. High sensitivity is not necessary for fuel dilution detection, as the sample size and other operating parameters can be altered to increase the vapor concentration. It is only necessary that the response be repeatable and reasonably rapid.

#### Water Sensor

The surface acoustic wave water sensor was only recently received due to delays in its development. One coating was applied and subjected to calibration. The sensitivity was found to be relatively low, the limit of detectability being a few thousand ppm. It should have been about 100 ppm with an optimum coating.

For the sample volumes and air flow rates used for the fuel dilution detection, this sensitivity does not appear to be adequate. If the oil sample contained 1 ppt liquid water, the lower limit of interest, the sensor would have to have a sensitivity of about 1 ppm to detect it in the vapor phase. The newest 290 MHz SAW sensors have attained this degree of sensitivity (6) but interference from the much larger hydrocarbon vapor concentration may be a problem. The addition of some separation technique or modification of the procedure may be necessary to successfully detect water at low concentrations.

#### CONCLUSIONS

The technique of detecting fuel dilution in diesel engine lubricants by heating a sample and electronically detecting the resulting vapors has been shown to be feasible. The volatilities of the fuels and lubricants are sufficiently different that a simple, indiscriminate sensor can detect 1% fuel dilution. The precision of the present laboratory implementation was limited by the characteristics of the tin oxide sensor used.

The surface acoustic wave sensor may provide a more stable and precise means of measuring the hydrocarbon vapor concentrations. An available SAW sensor can be coated with hydrocarbon-sensitive polymer films to determine its suitability.

Detecting small quantities of water in the presence of large amounts of hydrocarbon vapors may be difficult, but should be possible with sensors having improved sensitivity and discrimination.

### REFERENCES

1. Wohltjen, H., Jarvis, N.L., and Mowery, R.L., "Microsensors for Monitoring Lubricant Condition," NRL Research Proposal #61-T-153-4 of 23 January 1984.
2. Bolster, R.N., and Wohltjen, H., "A Simple Electronic Apparatus for Determining the Oxidation Stability of Lubricants and Other Organic Compounds," NRL Memorandum Report 5451, 28 September 1984.
3. Bolster, R.N., and Wohltjen, H., "Electronic Detection of Synthetic Lubricant Oxidative Breakdown," ASLE Trans. 29, pp. 377-382 (1986).
4. Clifford, P.K., and Tuma, D.T., "Characteristics of Semiconductor Gas Sensors," Part I, Sensors and Actuators, 3, pp. 233-254, (1982/83).
5. Wohltjen, H., "Mechanism of Operation and Design Considerations for Surface Acoustic Wave Device Vapour Sensors," Sensors and Actuators, 5, pp. 307-325 (1984).
6. Wohltjen, H., Snow, A.W., Barger, W.R. and Ballantine, D.S., "Trace Chemical Vapor Detection Using SAW Delay Line Oscillators," to be published in IEEE Trans.
7. Ballantine, D.S., Rose, S.A., Grate, J.W., and Wohltjen, H., "Correlation of SAW Coating Responses with Solubility Properties and Chemical Structure Using Pattern Recognition," NRL Memorandum Report 5813, 29 August 1986.

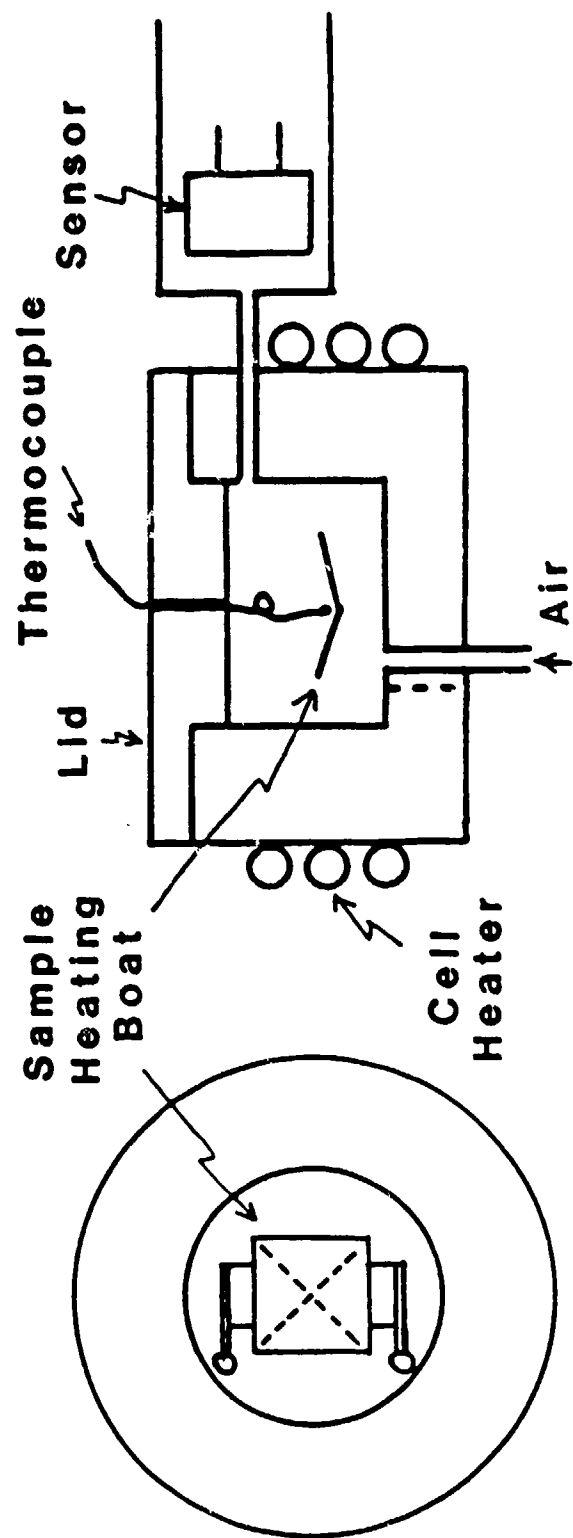


Fig. 1. Laboratory lubricant test cell with sample heating boat, thermocouple, and hydrocarbon sensor.

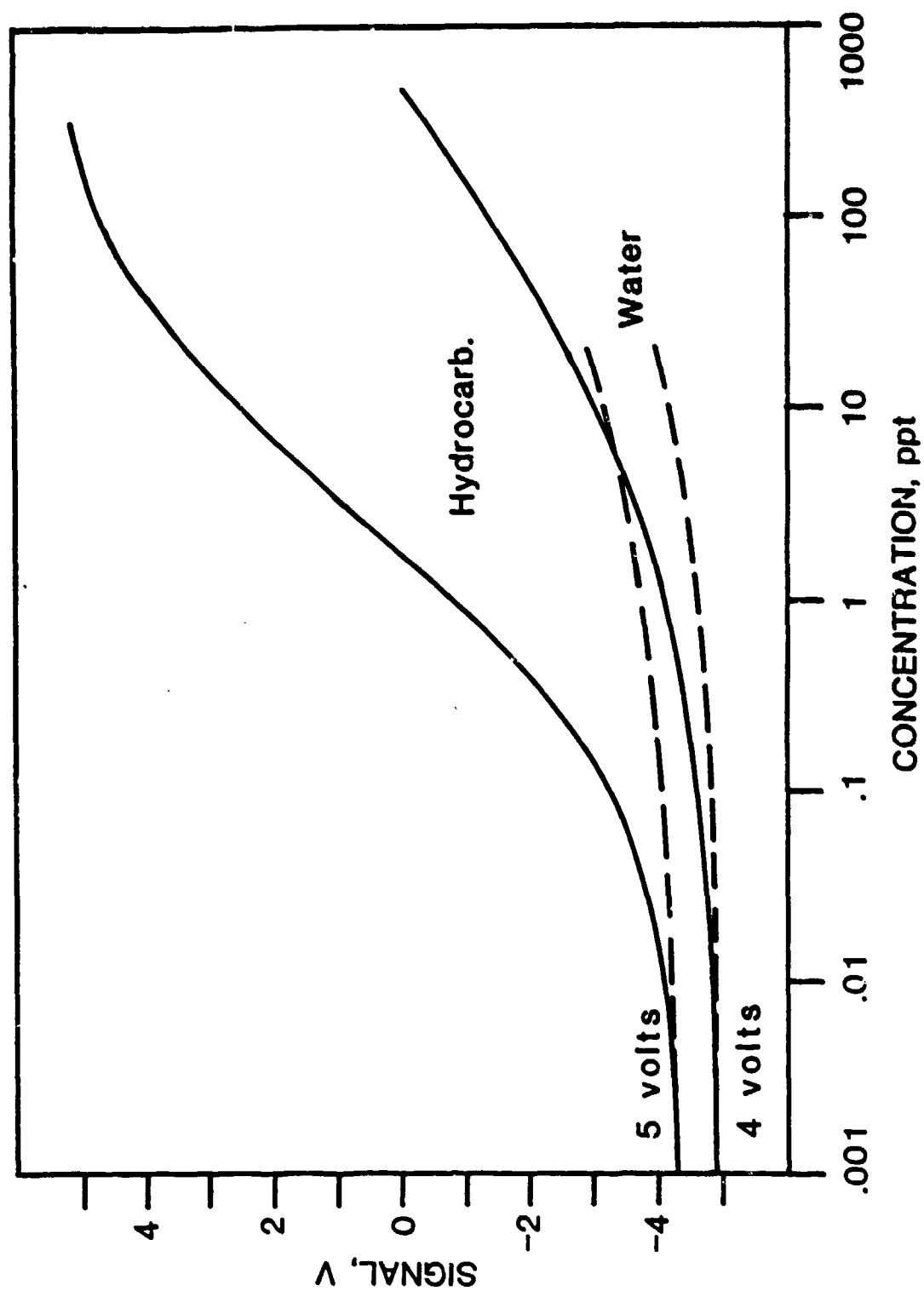


Fig. 2. Sensor calibration curves for hydrocarbon (solid lines) and water (dashed lines) vapors in air at two supply voltages.

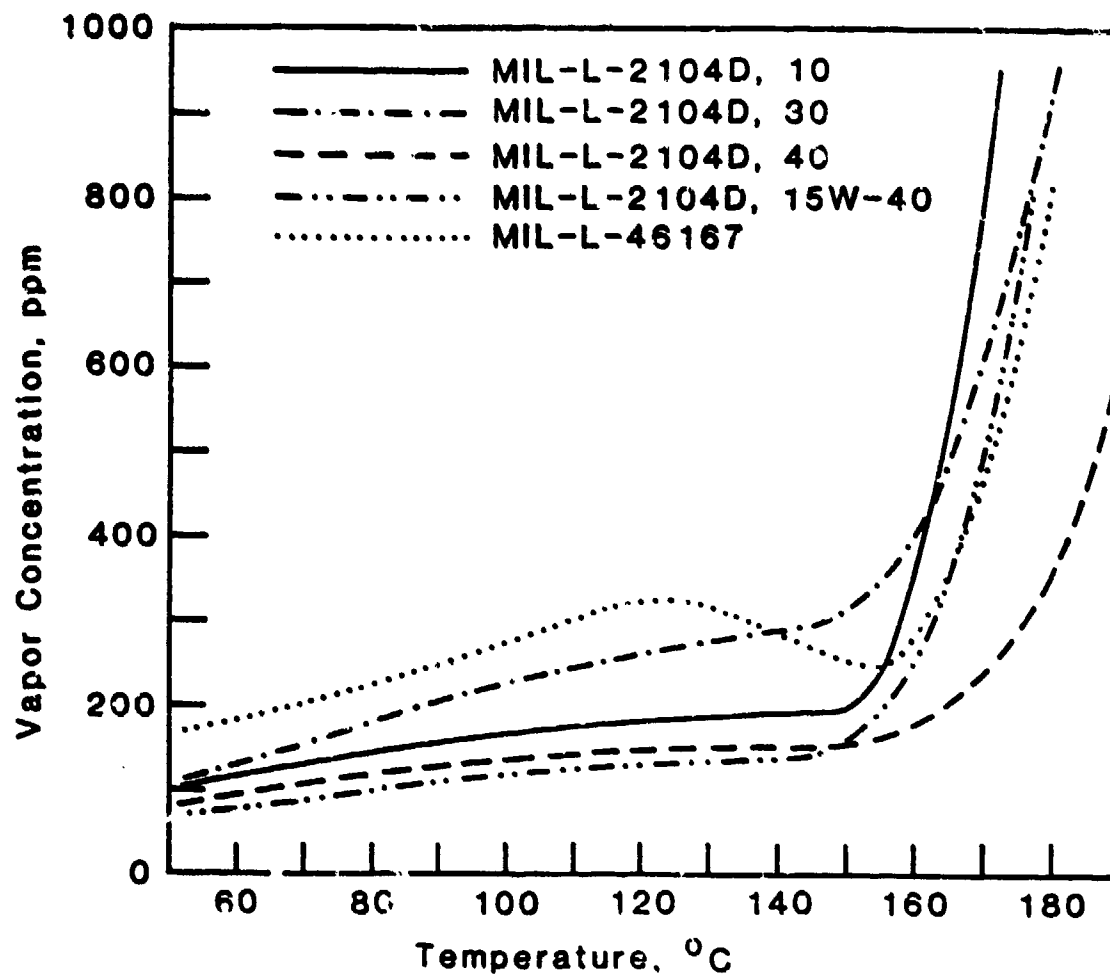


Fig. 3. The volatilities of five diesel engine lubricants. Samples of 20 microliters heated at 20°C per minute.

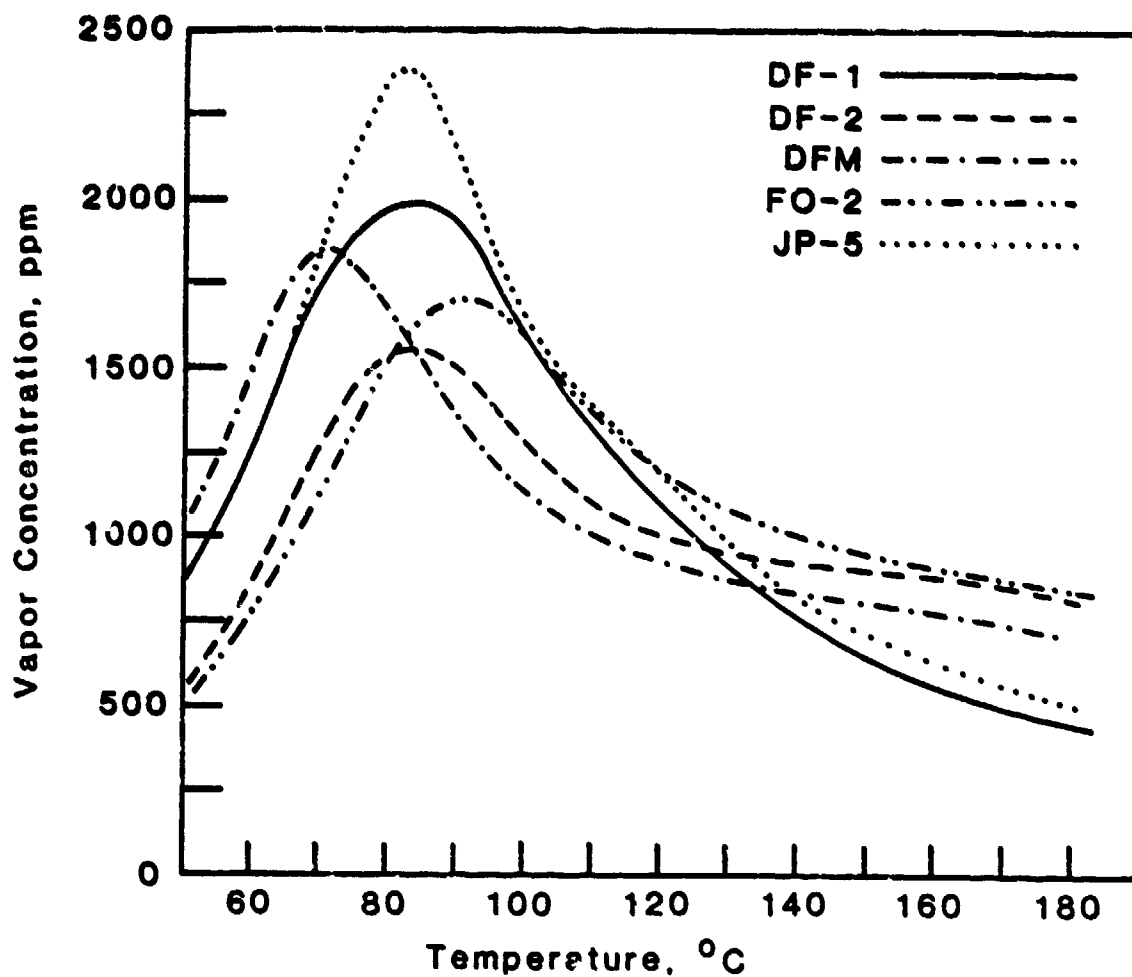


Fig. 4. The volatilities of five fuels. Samples of 5 microliters heated at 10°C per minute.

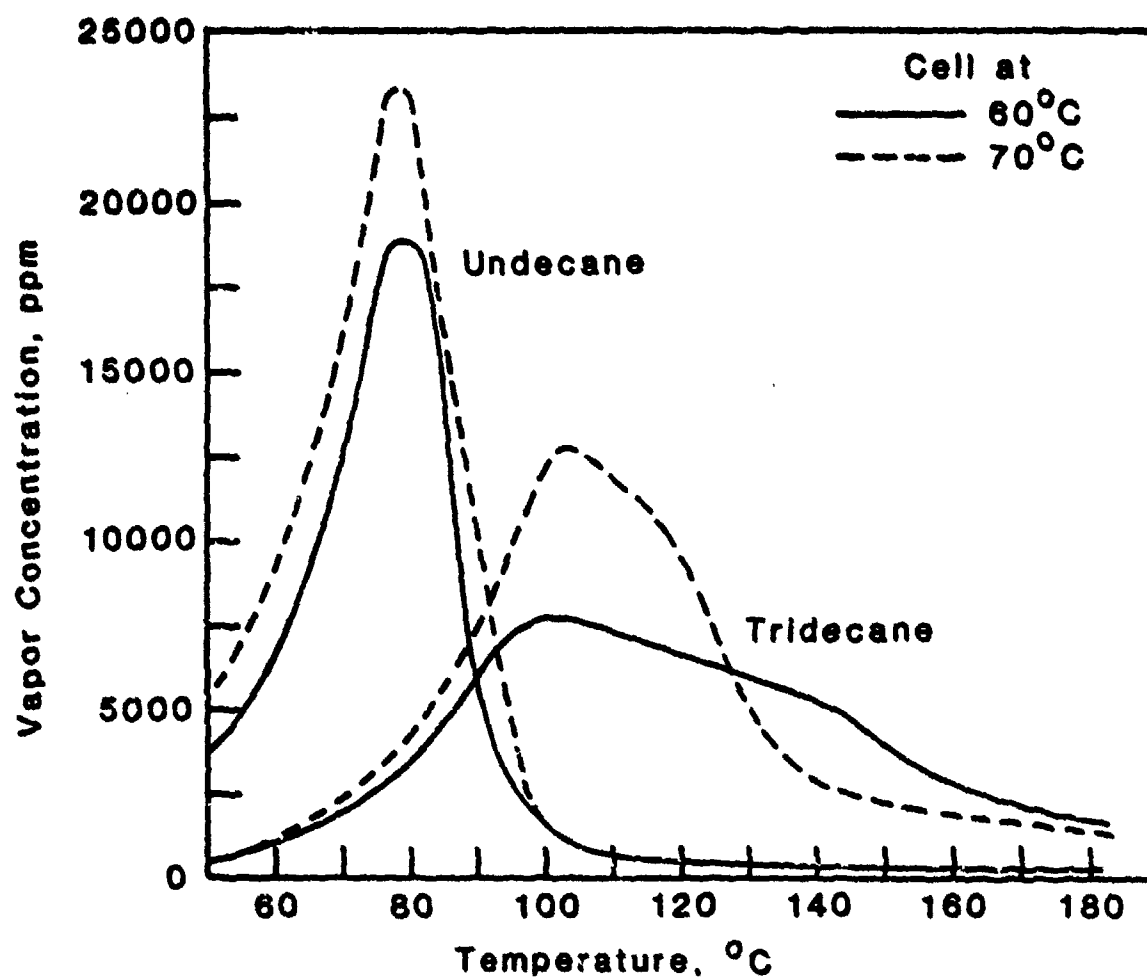


Fig. 5. The volatilities of undecane and tridecane at two cell temperatures. Samples of 5 microliters heated at 10°C per minute.



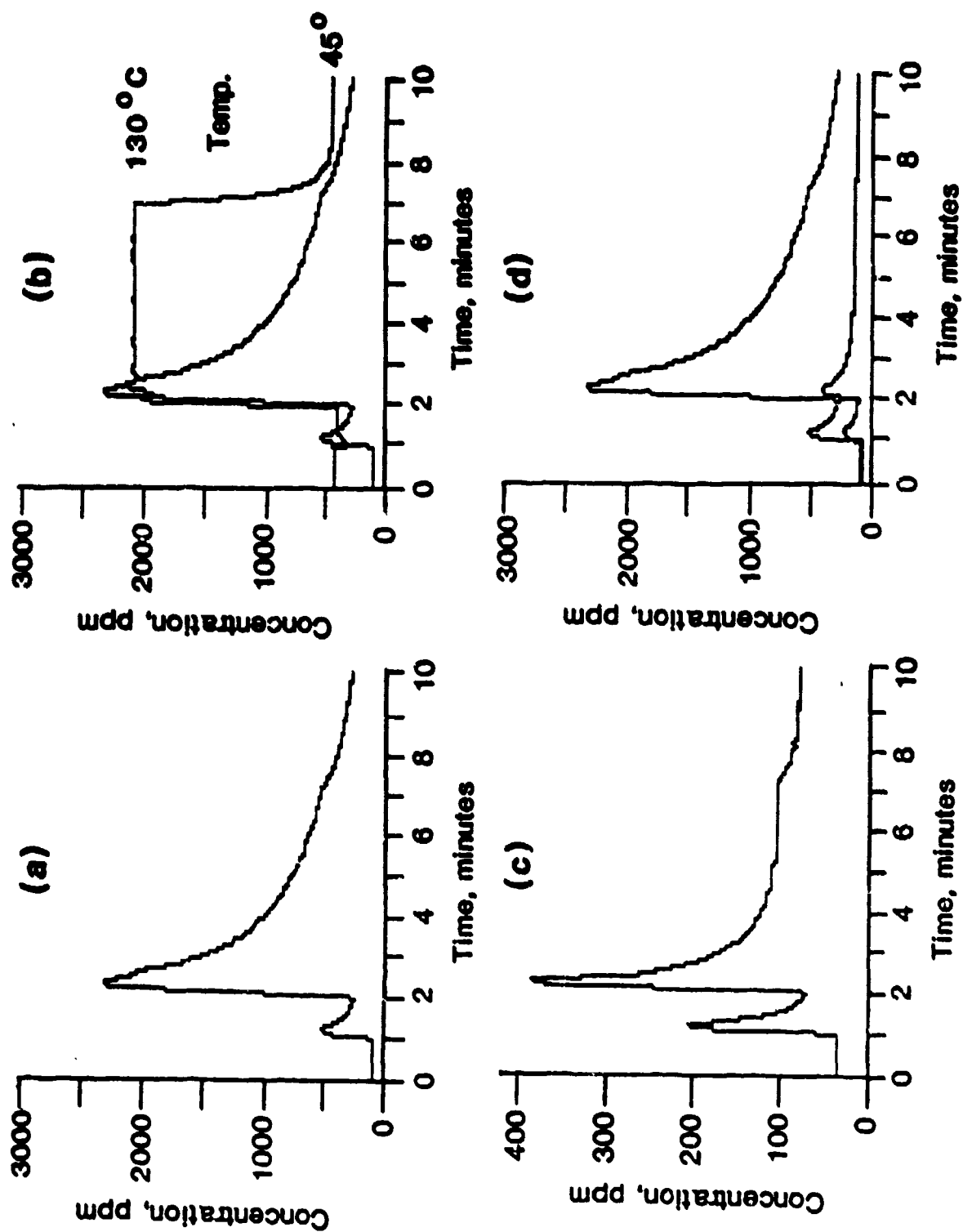


Fig. 6. (a) concentration vs. time plot of test run on 15W-40 with 5% DF-1; (b) Plot (a) with sample temperature vs. time plot superimposed; (c) Concentration vs. time plot of test run on neat 15W-40 oil; (d) Plots (a) and (c) superimposed at the same scale to show the change due to the presence of the fuel.